

# Synthesis and Thermoelectric Properties of $\text{CoP}_3$

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## ABSTRACT

In an effort to expand the range of operation for highly efficient, segmented thermoelectric unicouples currently being developed at the Jet Propulsion Laboratory (JPL), skutterudite phosphides are being investigated as potential high temperature segments to supplement antimonide segments that limit the use of these unicouples at a hot-side temperature of about 873-973 K. We report here on the synthesis and transport properties of one of these phosphide skutterudite materials,  $\text{CoP}_3$ . Large amounts of cobalt triphosphide have been prepared by direct reaction from stoichiometric powders at synthesis temperatures ranging from 873 to 1223 K. The synthesized powders were analyzed by x-ray diffractometry and hot pressed at 1273 K. The samples were analyzed by microprobe analysis and electrical conductivity, Seebeck voltage and thermal conductivity measurements were performed. The thermoelectric properties are presented and discussed as a function of temperature up to 1000 K. Initial thermal stability results are presented to assess the potential of this material for high temperature operation.

## INTRODUCTION

Skutterudite compounds have shown significant promise for use in high efficiency thermoelectric devices [1-4]. Significant interest has been devoted over the past few years to study their electrical and thermal properties to improve the state of the art materials [5]. Phosphorus compounds have been successfully synthesized in small amounts using several techniques [6,7]. The synthesis of such compounds is challenging due to the high phosphorus vapor pressures and the incongruent melting of the materials and the potential for dissociating at the high synthesis temperatures [8]. Large amounts of  $\text{CoP}_3$  however have been synthesized using direct reaction of stoichiometric amounts of pure elemental mixtures. Direct synthesis was the selected process due to the potential for producing large amounts of product. This work discusses the process used to produce bulk  $\text{CoP}_3$  and presents initial electrical and thermal stability characteristics measurements.

## EXPERIMENTAL DETAILS

Stoichiometric amounts of cobalt and phosphorus were reacted using a direct synthesis technique at temperatures ranging from 873 to 1223 K. High purity cobalt (99.995% at -22 mesh) was premixed with phosphorus (99.999% at -200 mesh) for 5 minutes in a polystyrene container using a high speed shaker. A uniform mixture of small grain size was used to allow the cobalt to take up the free phosphorus at a low enough temperature during the reaction to prevent the buildup of excessive pressures within the ampoule resulting in an explosion. A 3 g

mixture was then sealed under vacuum ( $< 1 \times 10^{-5}$  torr) in thick wall (1.5 mm) quartz ampoules. The ampoules were inserted into a furnace under nearly isothermal conditions ( $< 0.25$  °C/cm). Initially the samples were reacted over several temperature steps from a 473 K stabilization to a final soak at 1223 K. Later after examination of the results the final two steps were removed leaving a final soak at 873 K in an attempt to reduce the overall reaction time and temperature. The effect of reducing the final reaction temperature was to slightly increase the presence of a second phase comprised of CoP in the matrix. The full reaction path is shown in Table 1. Rapid

Table 1. Temperature reaction steps used to synthesize CoP<sub>3</sub>.

Steps	Conditions
1	473 K stabilization – 2hrs
2	9 K/hr ramp to 673 K
3	673 K reaction – 48 hrs
4	5 K/hr ramp to 873 K
5	873 K reaction – 120 hrs
6	5 K/hr ramp to 1223 K
7	1223 K reaction – 168 hrs
8	Rapid cooling at $> 100$ K/hr

cooling at the end of the process is achieved by stopping the furnace and allowing the samples to cool in an unrestrictive manner. Electrical measurements so far have only been made on material reacted at 1223 K using all steps noted in Table 1.

X-ray diffraction analysis was conducted on the samples after crushing and mixing the sintered product using an agate mortar and pestle. Electron beam microscopy was performed after hot pressing the mixed product at a temperature of 1273 K for 2 hrs 45 min under argon at 1500 kg pressure. The hot pressed samples were in the form of pellets 1.2 cm in diameter and about 1.2 cm long. The pellets were then sliced into 3 mm thick pieces for analysis. Density measurements conducted on the hot-pressed CoP<sub>3</sub> samples were in the range of 4.40 to 4.43 g/cm<sup>3</sup> compared with the theoretical density of 4.414 g/cm<sup>3</sup>. Variation from the theoretical value is attributable to the affects of porosity to a slight presence of CoP which at 6.417 g/cm<sup>3</sup> [9] is more dense than CoP<sub>3</sub>. No attempt was made at this time to sieve the final product to reduce the grain size prior to hot pressing so as to increase the density of the final sample.

Samples reacted to 1223 K were determined to be single phase CoP<sub>3</sub> showing only insignificant amounts of CoP. The very small amount of CoP present was attributed to a slight loss of phosphorus at the walls of the quartz ampoule. Pre-coating the inner ampoule walls with a thin carbonized layer by heating a small amount of acetone under a slight vacuum is expected to reduce the already small CoP presence. Figure 1 shows a 40x microprobe of a sample reacted to 1223 K. The gray regions are areas with various degrees of porosity of single phase CoP<sub>3</sub>. The gradations in the dark regions result from various sizes and densities of pores in the single CoP<sub>3</sub> matrix. Sieving the mixture prior to hot pressing is expected to reduce the overall pore density. The dark region at the lower edge of the photo marks the edge of the sample. The small white area was determined by electron microprobe to be CoP. Most of the sample however

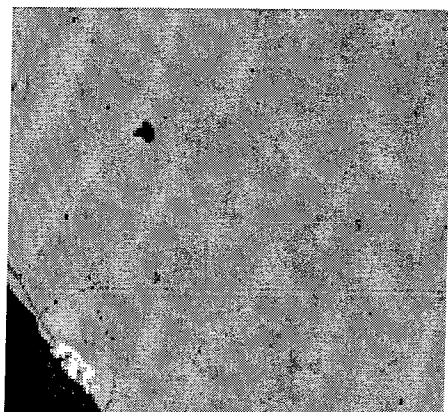


Figure 1. Microprobe of 1273 K hot pressed  $\text{CoP}_3$  sample with a small, more dense, CoP inclusion (white). The sample was grown at 950 °C using the process described in Table 1. The dark regions are voids and porous areas and the edge of the sample.

shows no presence of CoP. Corresponding X-ray diffraction results for this sample are presented in figure 2. Only minor CoP peaks are observed.

Reacting the stoichiometric mixture only up to 873 K produced a small increase in the presence of CoP in the overall matrix and had the benefit of significantly reducing the overall reaction time. The preparation process for this sample was the same as that for the 1223 K sample except that steps 6 and 7 in Table 1 were removed. Figure 3 is a 40x micrograph of a hot pressed 873 K reaction sample. A few larger regions of CoP can be observed for the 873 K sample. Further tests are needed to determine how the presence of the additional CoP will affect the electrical properties of the overall  $\text{CoP}_3$  matrix. Our results however indicate that extending the reaction at 873 K might further reduce the CoP presence.

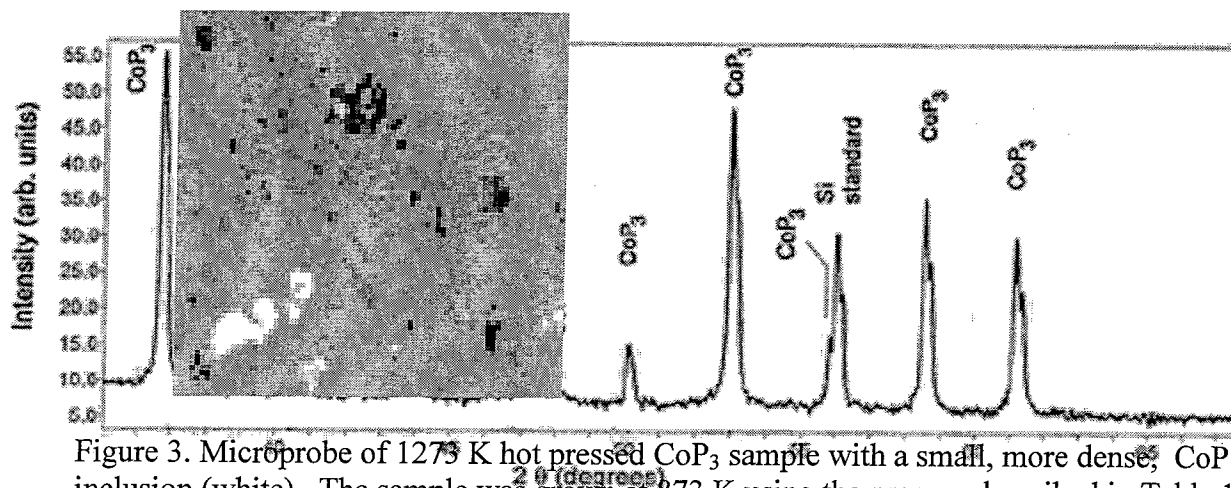


Figure 3. Microprobe of 1273 K hot pressed  $\text{CoP}_3$  sample with a small, more dense, CoP inclusion (white). The sample was grown at 873 K using the process described in Table 1. The dark regions are voids and porous areas and the edge of the sample.

Figure 2. X-ray diffraction micrograph showing  $\text{CoP}_3$  peaks along with a negligible amount of CoP. The Si standard peaks are used as a reference for sample identification.

## RESULTS AND DISCUSSION

### A. Electrical Properties

The properties of the  $\text{CoP}_3$  sample measured from room temperature up to the 800 to 1000 K range are shown in figures 4 through 7. The electrical measurements are compared with those of a  $\text{CoP}_3$  sample synthesized recently at Stanford and measured at JPL [7]. Both samples show p-type conductivity. The JPL sample exhibits an electrical resistivity comparable to that of the Stanford sample. The JPL sample also exhibits a lower room temperature mobility and corresponding carrier concentration than the Stanford sample. The higher temperature properties show more agreement. Close agreement is expected since both sample were synthesized using a similar process at a temperature of 1223 K. Another skutterudite,  $\text{CoSb}_3$ , is compared to the  $\text{CoP}_3$  electrical results in figures 4 and 5 [10]. The

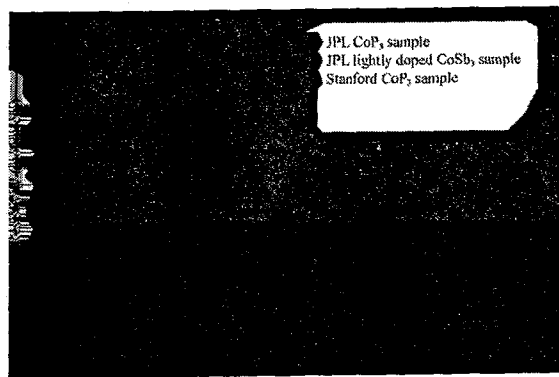


Figure 4. Temperature dependent resistivity measurement for undoped  $\text{CoP}_3$  sample grown at 1223 K.

electrical resistivity and corresponding mobility values for  $\text{CoSb}_3$  are higher than those for the  $\text{CoP}_3$  primarily due to the difference in carrier concentration, being two order of magnitude lower for the  $\text{CoSb}_3$  sample as observed in figure 6 [10].

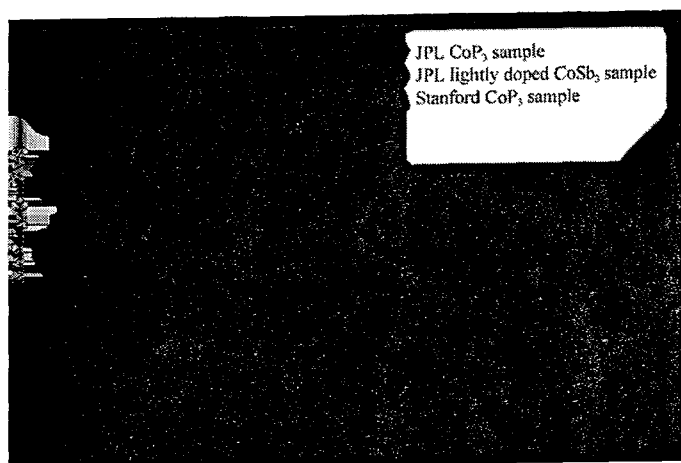


Figure 5. Temperature dependent mobility measurement for undoped  $\text{CoP}_3$  sample grown at 1223 K.

Figure 7 compares the thermal conductivity values for all three samples. The JPL and Stanford sample are in close agreement. The values for the  $\text{CoSb}_3$  sample are lower which can be expected considering the larger anionic mass for the  $\text{CoSb}_3$  sample, resulting in increased

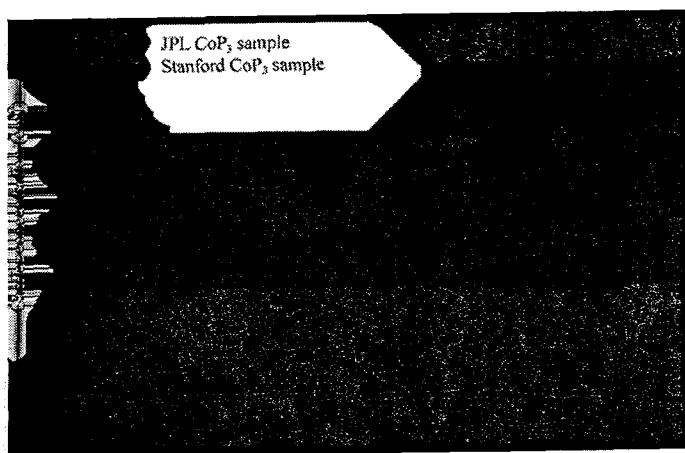


Figure 6. Temperature dependent carrier concentration measurement for undoped  $\text{CoP}_3$  sample grown at 1223 K.

phonon scattering. p-type  $\text{CoP}_3$  offers limited prospects for achieving high thermoelectric figures of merit at elevated temperatures primarily because of the low hole effective mass resulting in relatively low Seebeck coefficient [7] and high thermal conductivity. Provided n-type  $\text{CoP}_3$  samples can be produced by doping, these materials can potentially have relatively high ZT values at high temperatures considering that high electron effective mass can be obtained and significant reduction in lattice thermal conductivity as a result on electron-phonon scattering in heavily doped samples. Similar trends have been observed for n- and p-type  $\text{CoSb}_3$  [10]. Doping experiments for  $\text{CoP}_3$  are currently in progress at JPL.

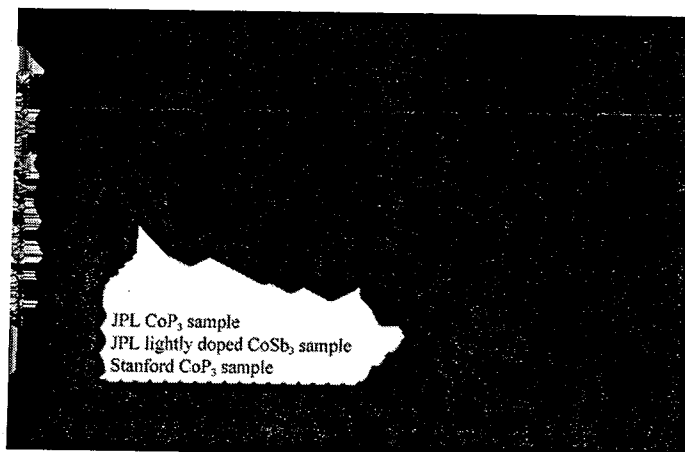


Figure 7. Temperature dependent thermal conductivity measurement for undoped  $\text{CoP}_3$  sample grown at 1223 K.

## B. Thermal Stability

Samples of  $\text{CoP}_3$  were annealed in static vacuum under both a temperature gradient and under isothermal conditions to determine the stability behavior. The samples were placed in 35 cm long quartz ampoules instrumented with two thermocouples separated by 4 cm at the location of the sample. For the gradient test the outer end of the ampoule extended outside the furnace so as to allow any evolving species to condense away from the sample. The gradient test had a value of 39 K/cm across the sample. In the case of the isothermal test, the entire ampoule was inserted into a three zone furnace that was adjusted to minimize any temperature gradient. The ampoule was instrumented with thermocouples in the same manner as the gradient test. The isothermal test had less than a 0.25 K/cm variation that increased away from the sample towards the outer end of the ampoule. Figure 8 shows the mass loss rate for each of these tests. Although the mass loss in the isothermal test is much less than the gradient test the proportional increase is the

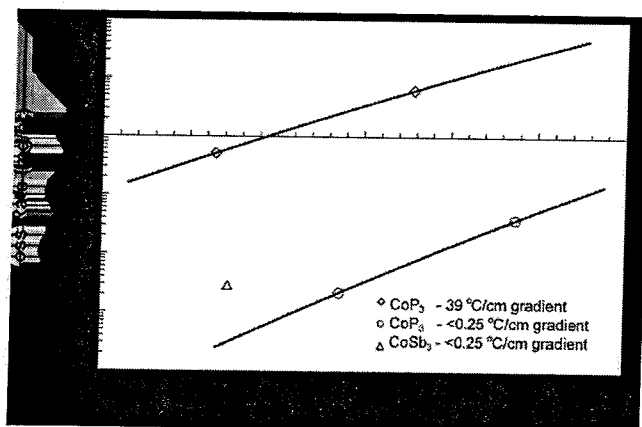


Figure 8. Mass loss rate for  $\text{CoP}_3$  in vacuum under a 39 K/cm temperature gradient and under a near isothermal 0.25 K/cm condition.

same. The similar proportional increase likely results from the porosity of the samples that keeps the mass loss from being diffusion limited. Comparative results from a  $\text{CoSb}_3$  sample included in figure 8 indicate a ten times increase in loss rate over  $\text{CoP}_3$  under isothermal conditions [11]. Microprobe analysis of the surface on the annealed sample subjected to the large thermal gradient related mass loss was determined to be uniform  $\text{CoP}$ . Cross-sectional microprobe analysis indicated that the  $\text{CoP}$  conversion extended uniformly into the sample. Density measurements also indicated a 40% increase from the initial measured  $\text{CoP}_3$  density ( $4.41 \text{ g/cm}^3$ ) over a 26 hours period at 1078 K under the 39 K/cm gradient in figure 8. The increased density support a conversion to  $\text{CoP}$  which has a measured density of 6.417

## CONCLUSIONS

We have investigated the properties of p-type  $\text{CoP}_3$  grown by direct synthesis from a stoichiometric pure elemental mixture. The first electrical and thermal measurements on bulk samples of p-type material have been presented. The results show that high purity bulk  $\text{CoP}_3$  can be produced utilizing a direct reaction process. Thermal annealing tests however have indicated that  $\text{CoP}_3$  undergoes a progressive decomposition in vacuum under a temperature gradient at temperatures in excess of 953 K. This loss can potentially be minimized by further controlling the microstructure of the samples and by application of a sublimation coating assuming that the underlying phosphorus vapor pressure is not excessive.

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